

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 03-251661

(71)Applicant : NGK INSULATORS LTD

(22)Date of filing : 30.09.1991

(72)Inventor : WADA YUKIHISA

## (54) METHOD FOR BURNING CERAMICS HONEYCOMB STRUCTURE

## (57)Abstract:

PURPOSE: To improve strength and water absorption in low thermal expansion by extrusion molding a cordierite raw material to give a honeycomb structure and burning the honeycomb structure in a given atmosphere under a specific condition.

CONSTITUTION: Talc is blended with kaolin and a cordierite raw material in such a way that the composition consists of 42-56wt.% SiO<sub>2</sub>, 30-45wt.% Al<sub>2</sub>O<sub>3</sub> and 12-16wt.% Ago and a crystal phase comprises cordierite. The blend is mixed with a molding auxiliary and/or a hole forming agent, extrusion molded and dried to give a honeycomb structure. The honeycomb structure is burnt in a given atmosphere at ≤60° C/Hr rate of heating in a thermal shrinkage temperature range of 1,100-1,200° C, ≥80° C//Hr rate of heating in a solid phase reaction advancing temperature range of 1,200-1,300° C and ≤60° C/Hr rate of heating in a temperature range from ≥1,300° C to a retention temperature to advance a liquid phase reaction.

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CLAIMS

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[Claim(s)]

[Claim 1] The chemical composition of a principal component is 2:42 - 56 % of the weight of SiO (s), and aluminum 2O3. : 30 - 45 % of the weight, MgO : So that a crystal phase may consist mainly of cordierite at 12 - 16 % of the weight In the approach of preparing talc, a kaolin, and other cordierite-ized raw materials, and calcinating a honeycomb structure object under a predetermined ambient atmosphere and the condition of predetermined temperature after extrusion molding on a honeycomb structure object It is 60 degrees C/Hr about the programming rate of the temperature region as for which a honeycomb structure object carries out a heat shrink. It is 80 degrees C/Hr about the programming rate in the temperature region to which it considers as the following and the solid phase reaction of a honeycomb structure object goes. While considering as the above It is 60 degrees C/Hr about the programming rate in the temperature region to which a liquid phase reaction goes. The baking approach of the ceramic honeycomb structure object characterized by considering as the following.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the suitable baking approach to calcinate the honeycomb structure catalyst support of low-temperature expansibility about the baking approach of a nature of cordierite ceramic honeycomb structure object with the high intensity used for the catalyst support for purification of automobile exhaust.

[0002]

[Description of the Prior Art] In order to have manufactured the nature of cordierite ceramic honeycomb structure object conventionally, after carrying out extrusion molding of the ceramic \*\*\*\* which mixed and prepared the cordierite formation ceramic raw material, the shaping assistant, or the ostomy agent, and obtained it and producing a ceramic honeycomb Plastic solid, the produced ceramic honeycomb Plastic solid was calcinated at the continuous furnace or the independent furnace under predetermined temperature, and the final ceramic honeycomb structure object had been acquired.

[0003] The honeycomb structure object used for the catalyst support for automobile exhaust purification among ceramic honeycomb structure objects is expensive in water absorption in order to raise the support engine performance of a catalyst, and in order to raise thermal shock resistance further, coefficient of thermal expansion must be low. In order to make a product property into a proper value conventionally, the maximum temperature at the time of baking and its holding time were controlled.

[0004]

[Problem(s) to be Solved by the Invention] Since what is necessary is just to make the porosity in a honeycomb rib high in order to make water absorption high when acquiring a honeycomb structure object by control of the maximum temperature mentioned above and its holding time, it is necessary to control sintering by lowering the maximum temperature at the time of baking, or shortening the holding time. On the other hand, since what is necessary is just to carry out eburation of the base in order to make coefficient of thermal expansion low, it is necessary to promote sintering by raising the maximum temperature at the time of baking, or lengthening the holding time.

[0005] Therefore, there was a problem which cannot make the optimal both the properties of high water absorption and a low coefficient of thermal expansion only by the maximum temperature at the time of baking and control of the holding time. Moreover, since the property was sharply changed by fluctuation of a raw material property, for example, grain size, mean particle diameter, etc., it was difficult to acquire each property with sufficient stability only by adjustment of the maximum-temperature holding time.

[0006] Moreover, although it was indicated that coefficient of thermal expansion can be made low by on the other hand making a programming rate quick on a target at the temperature of 1100 degrees C or more in JP,53-82822,A as a technique in which raw material adjustment attains low-temperature expansion-ization, it was inadequate as a means to attain the reduction in expansion, and high porosity to coincidence too.

[0007] The purpose of this invention tends to cancel the technical problem mentioned above, and tends to offer the baking approach of the ceramic honeycomb structure object which can optimize product properties, such as water absorption and coefficient of thermal expansion, to coincidence.

[0008]

[Means for Solving the Problem] The baking approach of the ceramic honeycomb structure object of this invention The chemical composition of a principal component is 2:42 - 56 % of the weight of SiO(s), and aluminum 2O3. : 30 - 45 % of the weight, MgO : So that a crystal phase may consist mainly of cordierite at 12 - 16 % of the weight In the approach of preparing talc, a kaolin, and other cordierite-ized raw materials, and calcinating a honeycomb structure object under a predetermined ambient atmosphere and the condition of predetermined temperature after extrusion molding on a honeycomb structure object It is 60 degrees C/Hr about the programming rate of the temperature region as for which a honeycomb structure object carries out a heat shrink. It is 80 degrees C/Hr about the programming rate in the temperature region to which it considers as the following and the solid phase reaction of a honeycomb structure object goes. While considering as the above It is 60 degrees C/Hr about the programming rate in the temperature region to which a liquid phase reaction goes. It is characterized by considering as the following.

[0009]

[Function] It sets in the configuration mentioned above and is 60 degrees C/Hr conventionally. The temperature up schedule which was carrying out the temperature up to retention temperature with the fixed programming rate It is 60 degrees C [ later than the conventional programming rate ]/Hr about for about 1100-1200 degrees C which is the temperature region as for which a honeycomb structure object carries out a heat shrink. It considers as the following. It is 80 degrees C [ quicker than the conventional programming rate ]/Hr about for about 1200-1300 degrees C which is the temperature region to which the solid phase reaction of a honeycomb structure object goes. While considering as the above 60 degrees C [ later than the programming rate of the former about 1300 degrees C or more which is the temperature region to which the liquid phase reaction of a honeycomb structure object goes ]/Hr By considering as the following, it found out that the product property of high water absorption and a low coefficient of thermal expansion which was not able to be attained to coincidence in the former could be fulfilled to coincidence.

[0010] That is, it is 60 degrees C/Hr about the programming rate of the temperature region for about 1100-1200 degrees C which carries out a heat shrink. In order that eburnation may progress slowly by making it low the following, it has contributed to achievement of a low-fever expansion coefficient. It is 80 degrees C/Hr about the programming rate of the temperature region to which the solid phase reaction between about 1200-1300 degrees C goes. By making it high with the above While controlling crystallization of the cordierite in the solid-phase-reaction condition which checks crystallization of the cordierite in the liquid phase reaction which is a main reaction which is not desirable and making it contribute to achievement of a low coefficient of thermal expansion and high water absorption It is 60 degrees C/Hr about the programming rate of the temperature region to which the liquid phase reaction to about 1300-degree-C or more retention temperature goes. By making it low the following, the desirable cordierite in the liquid phase reaction condition which is a main reaction was made to crystallize slowly, and it has contributed to achievement of a low coefficient of thermal expansion.

[0011] In addition, it is 60 degrees C/Hr about the programming rate of the base contraction temperature region for about 1100-1200 degrees C. In order that base contraction may carry out progress eburnation of the reason made into the following slowly by making the programming rate of this temperature region late, coefficient of thermal expansion falls. Moreover, when eburnation progresses, that to which a raw material grain spacing becomes small, cordierite-ization in a liquid phase reaction process tends to progress, and coefficient of thermal expansion falls by this, and the rate of an open pore (water absorption) becomes large is presumed. Moreover, a programming rate is 80 degrees C/Hr in the temperature region of this contraction process. Since a crack occurs in a Plastic solid according to the temperature gradient produced inside a Plastic solid when it is made quick with the above, it is effective to make a programming rate late also from this point.

[0012]

[Example] The ceramic honeycomb Plastic solid which applies the baking approach of this invention is the following, and can be made and acquired. First, point known as a presentation of the low expansion cordierite ceramics from the former forming [ cordierite theoretical ] (2MgO, 2aluminum2O3, and 5SiO2) 2:42 - 56 % of the weight of SiO(s) made into the core, They are 47 - 53

% of the weight, and aluminum 2O3 preferably. : They are 32 - 38 % of the weight, and MgO preferably 30 to 45% of the weight. : 12 to 16% of the weight, so that it may become 12.5 - 15% of the weight of a field preferably The talc, the kaolin, the alumina, and other cordierite-ized raw materials of a particle were prepared, and mixed kneading was carried out, and the shaping assistant and/or the ostomy agent were added to this mixture, and it plasticized possible [ extrusion molding ], it dried after extrusion molding on the honeycomb structure object, and the ceramic honeycomb structure object has been acquired.

[0013] As particle talc used, a thing especially with few alkali components is desirable. Moreover, on the occasion of atomization of talc and a kaolin, if temporary-quenching talc effective for control of the crack initiation of the honeycomb structure object by the contraction in the time of desiccation and baking etc. and a temporary-quenching kaolin are used, it will be good and the grain size at this time will use the same particle object as a raw raw material. In addition, it is desirable to choose what chooses the thing suitable for an application as a shaping assistant, for example from organic binders, such as methyl cellulose, a carboxymethyl cellulose, polyvinyl alcohol, starch paste, wheat flour, and a glycerol, a surfactant, a wax, etc., and suits, for example out of graphite, starch, a sawdust, etc. as an ostomy agent.

[0014] Then, it hits calcinating the acquired ceramic honeycomb structure object, and the usual temperature up is 60 degrees C/Hr as usual. While carrying out a temperature up to retention temperature, for example, 1410 degrees C It is 60 degrees C/Hr about the programming rate of the temperature region as for which the honeycomb structure object in a temperature up carries out a heat shrink. It considers as the following. It is 80 degrees C/Hr about the programming rate in the temperature region which is about 1200-1300 degrees C to which the solid phase reaction of a honeycomb structure object progresses. It is 60 degrees C/Hr about the programming rate in the temperature region which is about 1300-1400 degrees C to which it considers as the above and a liquid phase reaction progresses further. It is considering as the following.

[0015] Hereafter, an actual example is explained.

From example talc, a kaolin, and an alumina raw material, a ceramic raw material is prepared and mixed, methyl cellulose is added to the obtained mixture as a shaping assistant, it plasticizes, and the honeycomb Plastic solid fabricated and dried is prepared so that chemical composition may consist of the quality of cordierite. The configuration of a honeycomb Plastic solid is 80mm x die length of 150mm of x minor axes the major axis of 150mm. It is an elliptic-cylinder configuration and two or more honeycomb Plastic solids of the same configuration were manufactured.

[0016] First, in order to investigate the effect of the programming rate at the time of baking to a honeycomb Plastic solid, Lay the acquired honeycomb Plastic solid on the shelf board of muffle kiln, and it calcinates by changing the programming rate in the temperature region which is about 1300-1400 degrees C to which the temperature region and liquid phase reaction which are about 1200-1300 degrees C to which about 1100-1200-degree-C temperature region and solid phase reaction which carry out a heat shrink as shown in Table 1 progress progress. The various properties which a honeycomb structure object is acquired and show it in Table 1 to the acquired honeycomb structure object were measured, and the effect was investigated. In addition, it is temperature fall rate after carrying out temperature up, reaching retention temperature of 1410 degrees C and holding at this temperature for 4 hours 150 \*\*/Hr. It was made to descend. The coefficient of thermal expansion measured the coefficient of thermal expansion of 40 - 800 \*\* in the honeycomb direction of extrusion. Water absorption is 2 1cm, after carrying out dipping for 2 minutes into aqueous [ 30-degree C ] as a simulation of the approach of performing catalyst support. Weight percent: (water absorption Ushiro [ Shigekazu ]-dry weight) / dry weight x100 It asked. [ as opposed to honeycomb structure object dry weight for the coefficient of water absorption after removing excessive moisture with the pressure air of hit 1.4kgf ] As evaluation of thermal shock resistance, it is each temperature (it is step-up of every 25 degrees C from 700 degrees C). When it took out to a room temperature after holding for 20 minutes among an electric furnace, the temperature from which the crack occurred and the tap tone turned into dulness was searched for. A result is shown in Table 1.

[0017]

[Table 1]

ヒートカーブ	通常焼成	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
昇温 速度 (℃ /Hr)	1100-1200 ℃	60	20	80	120	60	60	60	60	60
	1200-1300 ℃	60	60	60	60	20	80	120	60	60
	1300-1400 ℃	60	60	60	60	60	60	60	20	80
吸水率 (%)	18.3	19.0	17.7	17.5	17.0	18.7	19.5	18.0	18.5	19.0
気孔率 (%)	39.2	39.7	38.7	38.4	38.0	39.4	40.1	38.7	39.3	39.7
熱膨張係数 (×10 <sup>-6</sup> /℃)	0.55	0.52	0.60	0.70	0.75	0.48	0.43	0.50	0.62	0.65
耐熱衝撃温度 (℃)	800	850	775	750	700	875	925	875	775	775

[0018] They are usually a heat curve and a heat curve (1) inside as a result of Table 1, (2), (3) When the programming rate of a between is made later than the result of the various properties of the calcinated honeycomb structure object for about 1100-1200 degrees C, coefficient of thermal expansion serves as a fall inclination, and water absorption (porosity) is a upward tendency, and it is 60 degrees C/Hr about the programming rate in this temperature requirement. When it was the following, it turned out that a good property is acquired. Usually, a heat curve and a heat curve (4), (5), (6) When the programming rate for about 1200-1300 degrees C is made quicker than the result of the various properties of the calcinated honeycomb structure object, coefficient of thermal expansion serves as a fall inclination, and water absorption is a upward tendency, and it is 80 degrees C/Hr about the programming rate in this temperature requirement. When it was the above, it turned out that a good property is acquired.

[0019] Moreover, similarly they are usually a heat curve and a heat curve (7) inside as a result of Table 1, (8) (9) When the programming rate for about 1300-1400 degrees C is made quick, a coefficient of thermal expansion serves as a fall inclination from the result of the various properties of the calcinated honeycomb structure object, and it is 60 degrees C/Hr about the programming rate in this temperature requirement. When it was the following, it turned out that a good property is acquired.

[0020] It is 80 degrees C/Hr about the programming rate for [ the result of the above table 1 to ] 1200-1300 degrees C. While considering as the above, it is 60 degrees C/Hr about the programming rate for 1300-1400 degrees C. Based on anticipation that the heat curve made into the following is best, in the heat curve similarly shown in Table 2, the honeycomb Plastic solid was actually calcinated and the property was investigated like Table 1 to the acquired honeycomb structure object. A result is shown in Table 2.

[0021]

[Table 2]

ヒートカーブ	通常焼成	(10)	(11)	(12)	(13)	(14)	
昇温 速度 (℃ /Hr)	1100-1200 ℃	60	40	40	60	20	50
	1200-1300 ℃	60	80	90	100	120	120
	1300-1400 ℃	60	60	60	40	30	40
吸水率 (%)	18.3	19.0	19.3	19.5	19.7	19.5	
気孔率 (%)	39.2	39.7	39.9	40.1	40.4	40.1	
熱膨張係数 (×10 <sup>-6</sup> /℃)	0.55	0.48	0.46	0.45	0.38	0.40	
耐熱衝撃温度 (℃)	800	875	900	900	950	925	

[0022] The honeycomb structure object calcinated by heat curve (10) - (14) from the result of Table 2 is the usual heat curve and a heat curve in Table 1 (1). - (9) As compared with the calcinated honeycomb structure object, it turned out that a good property is acquired in all properties. In addition, the heat curve of the Table 1 and 2 mentioned above is shown in drawing 1 - drawing 4 so that the description of each heat curve may become clearer. a heat curve and a heat curve (1) usual to drawing 1 , (2), (3) A heat curve and a heat curve (4) usual to drawing 2 , (5), About (6), it is a heat curve and a heat curve (7) usual to drawing 3 , (8) (9) A heat curve and a heat curve (10) usual to drawing 4 , (11), (12) is shown, respectively.

[0023] Moreover, this application people are 60 degrees C/Hr about a programming rate in the temperature field for about 1100-1200 degrees C as for which a ceramic honeycomb structure object carries out a heat shrink in JP,2-255576,A previously. Although indicated about the point that a honeycomb structure object with good dimensional accuracy is acquired by considering as the following, if this technique is combined with the invention in this application, it is clear that a honeycomb structure object also with good dimensional accuracy can be acquired with a product property.

[0024]

[Effect of the Invention] According to the baking approach of the ceramic honeycomb structure object of this invention, so that clearly from the above explanation It is 60 degrees C/Hr about the programming rate in the temperature region as for which the honeycomb structure object which consists of quality of cordierite carries out a heat shrink. It is 80 degrees C/Hr about the programming rate in the temperature region to which it considers as the following and solid phase reaction goes. While considering as the above By making into below 60 degrees C / Hr the programming rate in the temperature region to which a liquid phase reaction goes, crystallization of cordierite can be controlled and the ceramic honeycomb structure object which has a low coefficient of thermal expansion and high water absorption can be acquired. Moreover, even if it changes a raw material property, each property can be acquired with sufficient stability by changing the combination of the programming rate in each aforementioned temperature region.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The usual heat curve and usual heat curve (1) in the baking approach of this invention, (2), It is the graph which shows (3).

[Drawing 2] The usual heat curve and usual heat curve (4) in the baking approach of this invention, (5), It is the graph which shows (6).

[Drawing 3] The usual heat curve in the baking approach of this invention, a heat curve (7), and (8), (9) It is the shown graph.

[Drawing 4] The usual heat curve and heat curve (10) in the baking approach of this invention, (11), It is the graph which shows (12).

[Drawing 5] It is the graph which shows the contraction curve of the honeycomb structure object of this invention.

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[Translation done.]



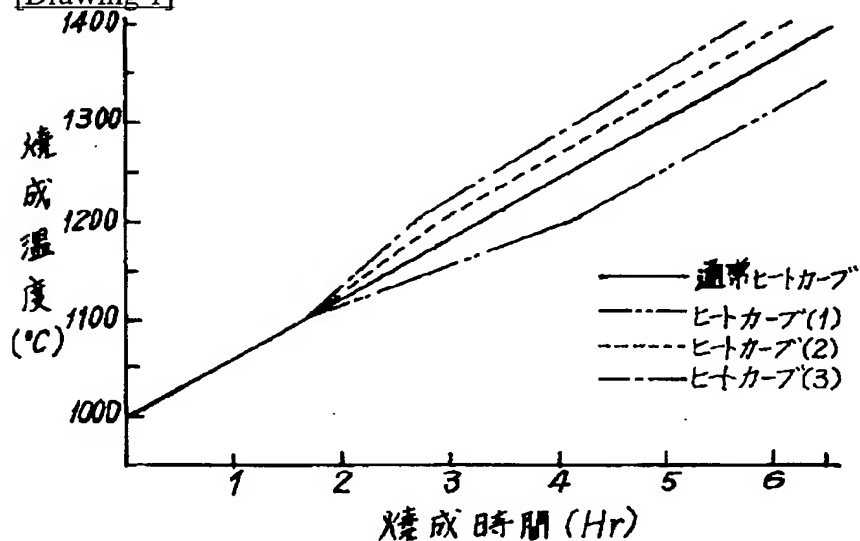
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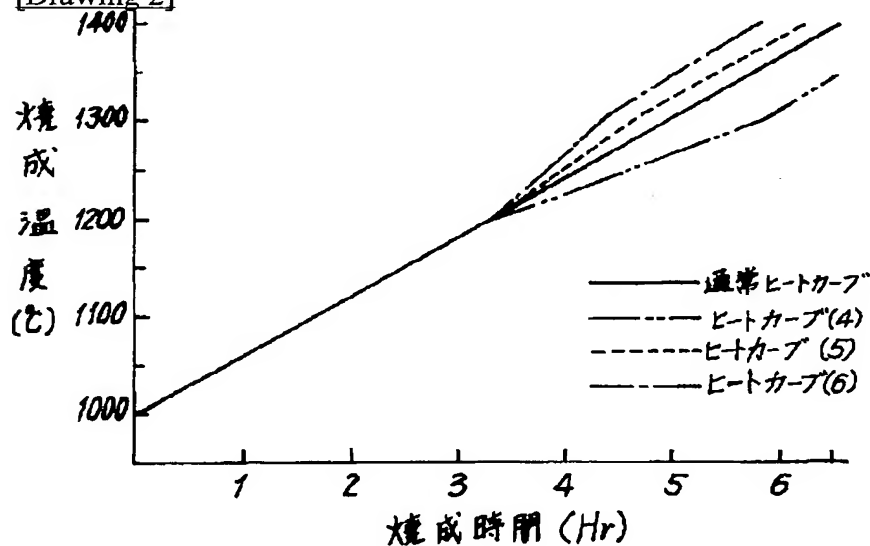
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## DRAWINGS

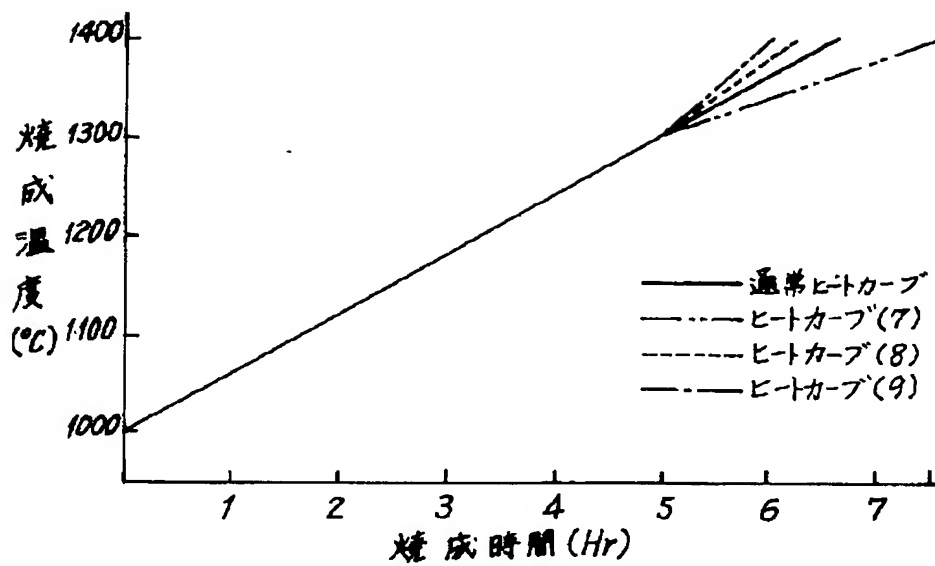
[Drawing 1]



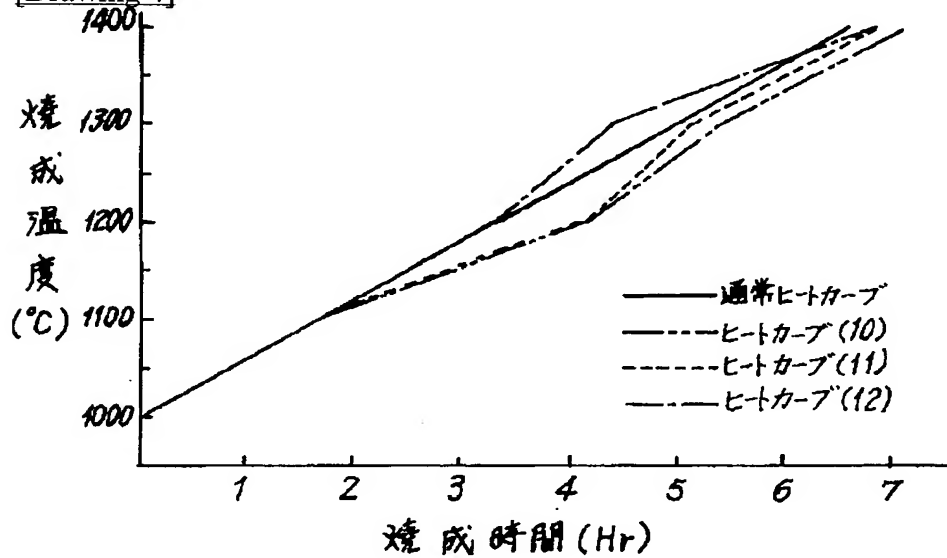
[Drawing 2]



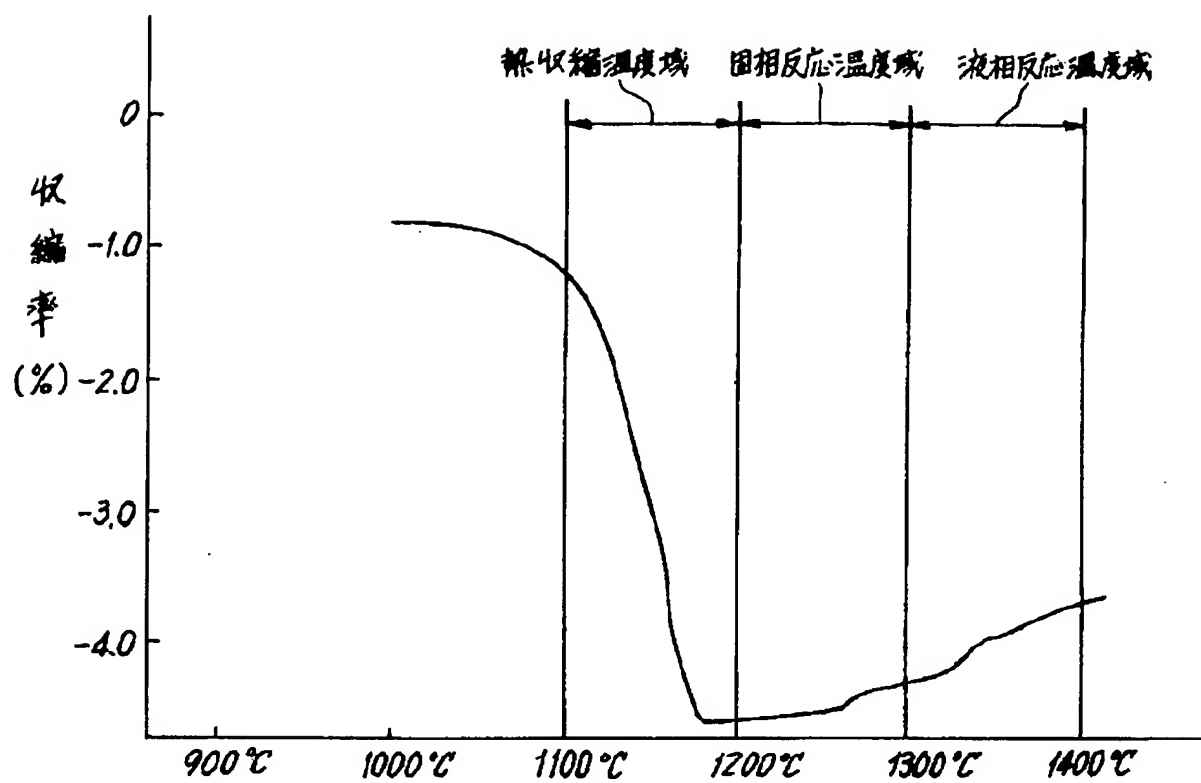
[Drawing 3]



[Drawing 4]



[Drawing 5]



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WRITTEN AMENDMENT

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----- [a procedure revision]

[Filing Date] October 6, Heisei 4

[Procedure amendment 1]

[Document to be Amended] Specification

[Item(s) to be Amended] 0011

[Method of Amendment] Modification

[Proposed Amendment]

[0011] In addition, it is 60 degrees C/Hr about the programming rate of the base contraction temperature region for about 1100-1200 degrees C. In order that base contraction may carry out progress eburnation of the reason made into the following slowly by making the programming rate of this temperature region late, coefficient of thermal expansion falls. Moreover, when eburnation progresses, that to which a raw material grain spacing becomes small, cordierite-ization in a liquid phase reaction process tends to progress, and coefficient of thermal expansion falls by this, and the rate of an open pore (water absorption) becomes large is presumed. Moreover, a programming rate is 80 degrees C/Hr in the temperature region of this contraction process. Since a dimension and deformation occur in a Plastic solid according to the temperature gradient produced inside a Plastic solid when it is made quick with the above, it is effective to make a programming rate late also from this point.

[Procedure amendment 2]

[Document to be Amended] Specification

[Item(s) to be Amended] 0016

[Method of Amendment] Modification

[Proposed Amendment]

[0016] First, in order to investigate the effect of the programming rate at the time of baking to a honeycomb Plastic solid, Lay the acquired honeycomb Plastic solid on the shelf board of muffle kiln, and it calcinates by changing the programming rate in the temperature region which is about 1300-1400 degrees C to which the temperature region and liquid phase reaction which are about 1200-1300 degrees C to which about 1100-1200-degree-C temperature region and solid phase reaction which carry out a heat shrink as shown in Table 1 progress progress. The various properties which a honeycomb structure object is acquired and show it in Table 1 to the acquired honeycomb structure object were measured, and the effect was investigated. In addition, it is temperature fall rate after carrying out temperature up, reaching retention temperature of 1410 degrees C and holding at this temperature for 4 hours 150 \*\*/Hr. It was made to descend. The coefficient of thermal expansion measured the coefficient of thermal expansion of 40 - 800 \*\* in the honeycomb direction of extrusion. Water absorption is 2 1cm, after carrying out dipping for 2 minutes into 30-degree C water as a simulation of the approach of performing catalyst support. Weight percent: (water absorption Ushiro [ Shigekazu ]-dry weight) / dry weight x100 It asked. [ as opposed to honeycomb structure object dry weight for the coefficient of water absorption after removing excessive moisture with the pressure air of hit 1.4kgf ] As evaluation of thermal shock resistance, it is each temperature (it is step-up of every 25 degrees C from 700 degrees C). When it took out to a room temperature after holding for 20 minutes among an electric furnace, the temperature from which the crack occurred

and the tap tone turned into dulness was searched for. A result is shown in Table 1.

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[Translation done.]

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3/26	A	7224-4G		
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35/64	C	7305-4G		

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(71)出願人 000004064

日本碍子株式会社

愛知県名古屋市瑞穂区須田町2番56号

(72)発明者 和田 幸久

愛知県愛知郡日進町大字梅森字株山110番  
地の812

(74)代理人 弁理士 杉村 暁秀 (外5名)

(54)【発明の名称】 セラミックハニカム構造体の焼成方法

(57)【要約】

【目的】 吸水率、熱膨張率等の製品特性を同時に最適化することのできるセラミックハニカム構造体の焼成方法を提供する。

【構成】 所定組成のコーージェライト原料をハニカム構造体に押し出し成形後の焼成を、ハニカム構造体の熱収縮する温度域の昇温速度を60°C/Hr 以下とし、ハニカム構造体の固相反応が進む温度域における昇温速度を80°C/Hr 以上とするとともに、液相反応が進む温度域における昇温速度を60°C/Hr 以下とする。

## 【特許請求の範囲】

【請求項1】 主成分の化学組成が $\text{SiO}_2$ ：42～56重量％、 $\text{Al}_2\text{O}_3$ ：30～45重量％、 $\text{MgO}$ ：12～16重量％で結晶相が主としてコーゼライトから成るように、タルク、カオリン及び他のコーゼライト化原料を調合しハニカム構造体に押し出し成形後、ハニカム構造体を所定の雰囲気、所定の温度の状態で焼成する方法において、ハニカム構造体の熱収縮する温度域の昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下とし、ハニカム構造体の固相反応が進む温度域における昇温速度を $80^\circ\text{C}/\text{Hr}$ 以上とするとともに、液相反応が進む温度域における昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下とすることを特徴とするセラミックハニカム構造体の焼成方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明はコーゼライト質セラミックハニカム構造体の焼成方法に関し、特に自動車排ガスの浄化用触媒担体に用いられる高強度で低熱膨張性のハニカム構造触媒担体を焼成するのに好適な焼成方法に関するものである。

## 【0002】

【従来の技術】従来、コーゼライト質セラミックハニカム構造体を製造するには、コーゼライト形成セラミック原料と成形助剤または造孔剤とを混合・調合して得たセラミック杯土を押し出し成形してセラミックハニカム成形体を作製した後、作製したセラミックハニカム成形体を所定温度下で連続炉または単独炉により焼成して最終的なセラミックハニカム構造体を得ていた。

【0003】セラミックハニカム構造体のうち、自動車排ガス浄化用触媒担体に使用されるハニカム構造体は、触媒の担持性能を高めるため吸水率を高く、さらに耐熱衝撃性を高めるため熱膨張率は低くしなければならない。従来、製品特性を適正值とするために、焼成時の最高温度およびその保持時間を制御していた。

## 【0004】

【発明が解決しようとする課題】上述した最高温度およびその保持時間の制御によりハニカム構造体を得る場合、吸水率を高くするためには、ハニカムリブ内の気孔率を高くすればよいので、焼成時の最高温度を下げるか保持時間を短くすることにより焼結を抑制する必要がある。一方、熱膨張率を低くするためには、素地を緻密化させればよいので、焼成時の最高温度を上げるか保持時間を長くすることにより焼結を促進する必要がある。

【0005】従って、焼成時の最高温度およびその保持時間の制御のみで、高い吸水率と低い熱膨張率の両特性を最適にすることができない問題があった。また、原料特性例えば粒度、平均粒径等の変動により特性が大きく変動することもあり、最高温度保持時間の調整のみでは各特性を安定性よく得ることは困難であった。

【0006】また、原料調整により低熱膨張化を達成する技術として、特開昭53-82822号公報において

$1100^\circ\text{C}$ 以上の温度で昇温速度を一方向的に速くすることにより熱膨張率を低くできることが開示されているが、やはり低膨張化と高気孔率を同時に達成する手段としては不十分であった。

【0007】本発明の目的は上述した課題を解消して、吸水率、熱膨張率等の製品特性を同時に最適化することのできるセラミックハニカム構造体の焼成方法を提供しようとするものである。

## 【0008】

【課題を解決するための手段】本発明のセラミックハニカム構造体の焼成方法は、主成分の化学組成が $\text{SiO}_2$ ：42～56重量％、 $\text{Al}_2\text{O}_3$ ：30～45重量％、 $\text{MgO}$ ：12～16重量％で結晶相が主としてコーゼライトから成るように、タルク、カオリン及び他のコーゼライト化原料を調合しハニカム構造体に押し出し成形後、ハニカム構造体を所定の雰囲気、所定の温度の状態で焼成する方法において、ハニカム構造体の熱収縮する温度域の昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下とし、ハニカム構造体の固相反応が進む温度域における昇温速度を $80^\circ\text{C}/\text{Hr}$ 以上とするとともに、液相反応が進む温度域における昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下とすることを特徴とするものである。

## 【0009】

【作用】上述した構成において、従来は例えば $60^\circ\text{C}/\text{Hr}$ の一定の昇温速度で保持温度まで昇温していた昇温スケジュールを、ハニカム構造体の熱収縮する温度域である約 $1100\sim 1200^\circ\text{C}$ 間を従来の昇温速度より遅い $60^\circ\text{C}/\text{Hr}$ 以下とし、ハニカム構造体の固相反応が進む温度域である約 $1200\sim 1300^\circ\text{C}$ 間を従来の昇温速度より速い $80^\circ\text{C}/\text{Hr}$ 以上とするとともに、ハニカム構造体の液相反応が進む温度域である約 $1300^\circ\text{C}$ 以上を従来の昇温速度より遅い $60^\circ\text{C}/\text{Hr}$ 以下とすることにより、高い吸水率と低い熱膨張率という、従来では同時に達成することのできなかった製品特性を同時に満たすことができることを見出した。

【0010】すなわち、約 $1100\sim 1200^\circ\text{C}$ 間の熱収縮する温度域の昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下と低くすることにより、ゆっくりと緻密化が進むため、低熱膨張率の達成に寄与している。約 $1200\sim 1300^\circ\text{C}$ の間の固相反応が進む温度域の昇温速度を $80^\circ\text{C}/\text{Hr}$ 以上と高くすることにより、主反応である液相反応でのコーゼライトの晶出を阻害する固相反応状態における望ましくないコーゼライトの晶出を抑制し、低い熱膨張率と高い吸水率の達成に寄与させるとともに、約 $1300^\circ\text{C}$ 以上保持温度までの液相反応が進む温度域の昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下と低くすることにより、主反応である液相反応状態における望ましいコーゼライトをゆっくりと晶出させ、低い熱膨張率の達成に寄与している。

【0011】なお、約 $1100\sim 1200^\circ\text{C}$ 間の素地収縮温度域の昇温速度を $60^\circ\text{C}/\text{Hr}$ 以下とする理由は、この温度域の昇温速度を遅くすることにより、素地収縮がゆっくり進み緻密化するため、熱膨張率は低下する。また、緻密化

が進むことにより原料粒子間隔が小さくなり、液相反応過程でのコーゼライト化が進み易く、これによって熱膨張率が低下し、また開気孔率（吸水率）が大きくなるものと推定される。また、この収縮過程の温度域で昇温速度が80°C/Hr以上と速くした場合、成形体内部に生じる温度差により成形体にクラックが発生することもあり、この点からも昇温速度を遅くすることが有効である。

【0012】

【実施例】本発明の焼成方法を適用するセラミックハニカム成形体は以下のようにして得ることができる。まず、従来から低膨張コーゼライトセラミックスの組成として知られているコーゼライト理論組成点（ $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ）を中心とした $\text{SiO}_2$ ：42～56重量%、好ましくは47～53重量%、 $\text{Al}_2\text{O}_3$ ：30～45重量%、好ましくは32～38重量%、 $\text{MgO}$ ：12～16重量%、好ましくは12.5～15重量%の領域となるように、微粒のタルク、カオリン、アルミナおよび他のコーゼライト化原料を調合し、混合混練し、この混合物に成形助剤および/または造孔剤を加えて押出成形可能に可塑化し、ハニカム構造体に押し出し成形後乾燥して、セラミックハニカム構造体を得ている。

【0013】使用される微粒タルクとしては特にアルカリ成分の少ないものが好ましい。また、タルク、カオリンの微粒化に際し、乾燥・焼成時での収縮等によるハニカム構造体の亀裂発生を抑制に効果的な仮焼タルク、仮焼カオリンを使用すると良好であり、このときの粒度は生原料と同様の微粒物を使用する。なお、成形助剤としては、例えばメチルセルロース、カルボキシメチルセルロース、ポリビニルアルコール、澱粉糊、小麦粉、グリセリンなどの有機バインダーや界面活性剤、ワックス等のなかから用途に合ったものを選択し、また造孔剤としては、例えばグラファイト、澱粉、おがくず等のなかから適合するものを選択するのが好ましい。

【0014】その後、得られたセラミックハニカム構造体を焼成するにあたり、通常の昇温は従来と同様に60°C/Hrで保持温度例えば1410°Cまで昇温するとともに、昇

温中ハニカム構造体の熱収縮する温度域の昇温速度を60°C/Hr以下とし、ハニカム構造体の固相反応が進む約1200～1300°Cの温度域における昇温速度を80°C/Hr以上とし、さらに液相反応が進む約1300～1400°Cの温度域における昇温速度を60°C/Hr以下としている。

【0015】以下、実際の例について説明する。

#### 実施例

タルク、カオリンおよびアルミナ原料から化学組成がコーゼライト質から成るようにセラミック原料を調合・混合し、得られた混合物に成形助剤としてメチルセルロースを加えて可塑化し、成形・乾燥したハニカム成形体を準備する。ハニカム成形体の形状は、長径150mm×短径80mm×長さ150mmの楕円柱形状であり、同じ形状のハニカム成形体を複数個製造した。

【0016】まず、ハニカム成形体に対する焼成時の昇温速度の影響を調べるため、得られたハニカム成形体をマッフル窯の棚板上に載置し、表1に示すように熱収縮する約1100～1200°C温度域および固相反応が進む約1200～1300°Cの温度域および液相反応が進む約1300～1400°Cの温度域における昇温速度を変えて焼成を行い、ハニカム構造体を得、得られたハニカム構造体に対し表1に示す各種特性を測定し、その影響を調べた。なお、昇温して保持温度1410°Cに達した後は、この温度で4時間保持した後、降温速度150°C/Hrで降温させた。熱膨張係数はハニカム押出方向における40～800°Cの熱膨張係数を測定した。吸水率は、触媒担持を行う方法の模擬として30°Cの水溶液中に2分間ディッピングした後1cm<sup>3</sup>当たり1.4kgfの圧力空気て余分な水分を除去した後の吸水量をハニカム構造体乾燥重量に対する重量百分率：（吸水後重量－乾燥重量）／乾燥重量×100で求めた。耐熱衝撃性の評価として、各温度（700°Cより25°Cずつのステップアップ）で電気炉中20分間保持した後室温に取り出した時クラックが発生し打音が濁音となった温度を求めた。結果を表1に示す。

【0017】

【表1】



ヒートカーブ		通常焼成	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
昇温速度 (°C/Hr)	1100-1200 °C	60	20	80	120	60	60	60	60	60	60
	1200-1300 °C	60	60	60	60	20	80	120	60	60	60
	1300-1400 °C	60	60	60	60	60	60	60	20	80	120
吸水率 (%)		18.3	19.0	17.7	17.5	17.0	18.7	19.5	18.0	18.5	19.0
気孔率 (%)		39.2	39.7	38.7	38.4	38.0	39.4	40.1	38.7	39.3	39.7
熱膨張係数 ( $\times 10^{-6}/^{\circ}\text{C}$ )		0.55	0.52	0.60	0.70	0.75	0.48	0.43	0.50	0.62	0.65
耐熱衝撃温度 (°C)		800	850	775	750	700	875	925	875	775	775

【0018】表1の結果中、通常ヒートカーブおよびヒートカーブ(1), (2), (3)で焼成したハニカム構造体の各種特性の結果より、約1100~1200°Cを間の昇温速度を遅くした場合、熱膨張率は低下傾向となり吸水率(気孔率)は増加傾向であり、この温度範囲での昇温速度を60°C/Hr以下とすると良好な特性が得られることがわかった。通常ヒートカーブおよびヒートカーブ(4), (5), (6)で焼成したハニカム構造体の各種特性の結果より、約1200~1300°C間の昇温速度を速くした場合、熱膨張率は低下傾向となり、吸水率は増加傾向であり、この温度範囲での昇温速度を80°C/Hr以上とすると良好な特性が得られることがわかった。

【0019】また、同じく表1の結果中、通常ヒートカーブおよびヒートカーブ(7), (8), (9)で焼成したハニ

\* カム構造体の各種特性の結果より、約1300~1400°C間の昇温速度を速くした場合、熱膨張係数が低下傾向となり、この温度範囲での昇温速度を60°C/Hr以下とすると良好な特性が得られることがわかった。

20 【0020】以上の表1の結果から、1200~1300°C間の昇温速度を80°C/Hr以上とするとともに、1300~1400°C間の昇温速度を60°C/Hr以下とするヒートカーブが最良であるとの予想に基づき、同様に表2に示すヒートカーブで実際にハニカム成形体を焼成し、得られたハニカム構造体に対し表1と同様にその特性を調べた。結果を表2に示す。

【0021】

【表2】

ヒートカーブ	通常焼成	(10)	(11)	(12)	(13)	(14)	
昇温速度 (℃ /Hr)	1100-1200 ℃	60	40	40	60	20	50
	1200-1300 ℃	60	80	90	100	120	120
	1300-1400 ℃	60	60	60	40	30	40
吸水率 (%)	18.3	19.0	19.3	19.5	19.7	19.5	
気孔率 (%)	39.2	39.7	39.9	40.1	40.4	40.1	
熱膨張係数 (×10 <sup>-6</sup> /℃)	0.55	0.48	0.46	0.45	0.38	0.40	
耐熱衝撃温度 (℃)	800	875	900	900	950	925	

【0022】表2の結果から、ヒートカーブ(10)~(14)で焼成したハニカム構造体は、通常のヒートカーブおよび表1中のヒートカーブ(1)~(9)で焼成したハニカム構造体と比較して、すべての特性において良好な特性が得られることがわかった。なお、各ヒートカーブの特徴がより明瞭になるように、上述した表1および表2のヒートカーブを図1~図4に示す。図1には通常のヒート

カーブとヒートカーブ(1), (2), (3)を、図2には通常のヒートカーブとヒートカーブ(4), (5), (6)を、図3には通常のヒートカーブとヒートカーブ(7), (8), (9)を、図4には通常のヒートカーブとヒートカーブ(10), (11), (12)をそれぞれ示す。

50 【0023】また、本願人は先に特開平2-255576号において、セラミックハニカム構造体が熱収縮する約1100~

1200°C間の温度領域にて、昇温速度を60°C/Hr以下とすることにより寸法精度の良好なハニカム構造体を得られる点について開示しているが、この技術を本願発明と組み合わせれば、製品特性とともに、寸法精度も良好なハニカム構造体を得ることができることは明らかである。

【0024】

【発明の効果】以上の説明から明らかなように、本発明のセラミックハニカム構造体の焼成方法によれば、コーゼライト質からなるハニカム構造体の熱収縮する温度域における昇温速度を60°C/Hr以下とし、固相反応が進む温度域における昇温速度を80°C/Hr以上とするとともに、液相反応が進む温度域における昇温速度を60°C/Hr以下とすることにより、コーゼライトの晶出を抑制し、低い熱膨張率と高い吸水率を有するセラミックハニカム構造体を得ることができる。また、原料特性が変動\*

\*しても前記の各温度域における昇温速度の組み合わせを変更することにより各特性を安定性良く得ることができる。

【図面の簡単な説明】

【図1】本発明の焼成方法における通常のヒートカーブとヒートカーブ(1)、(2)、(3)を示すグラフである。

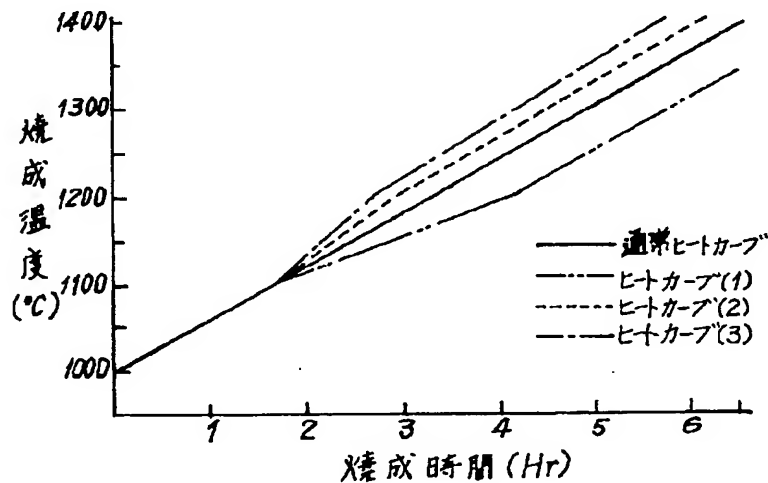
【図2】本発明の焼成方法における通常のヒートカーブとヒートカーブ(4)、(5)、(6)を示すグラフである。

【図3】本発明の焼成方法における通常ヒートカーブとヒートカーブ(7)、(8)、(9)を示すグラフである。

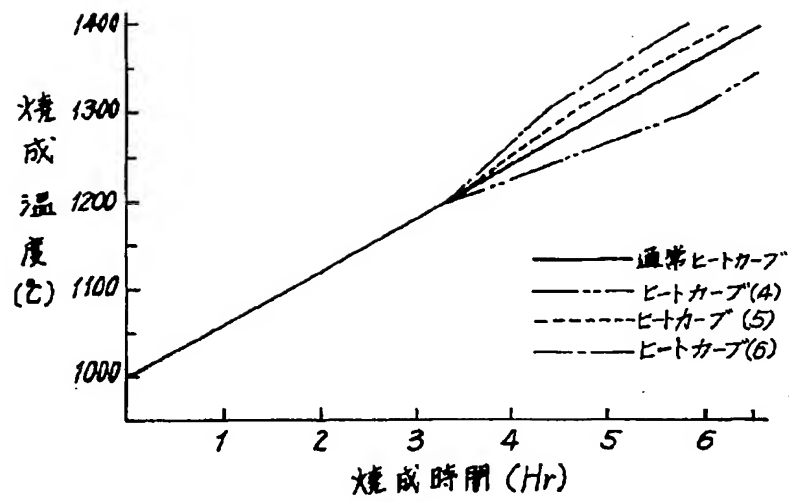
【図4】本発明の焼成方法における通常ヒートカーブとヒートカーブ(10)、(11)、(12)を示すグラフである。

【図5】本発明のハニカム構造体の収縮曲線を示すグラフである。

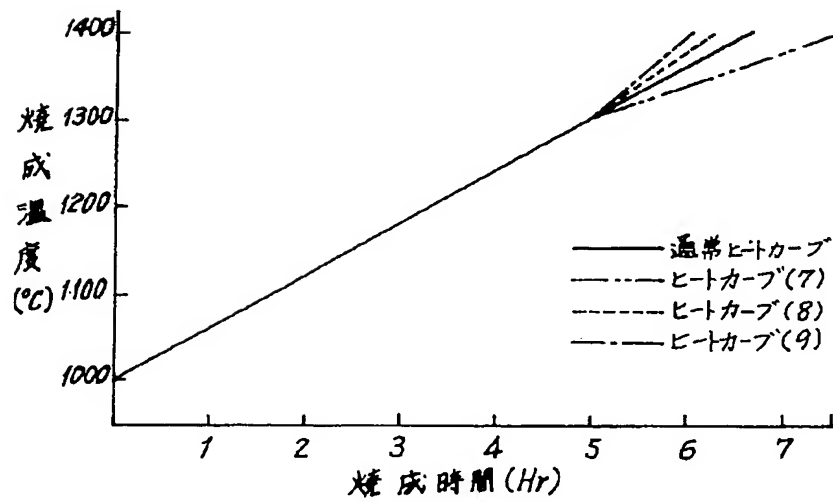
【図1】



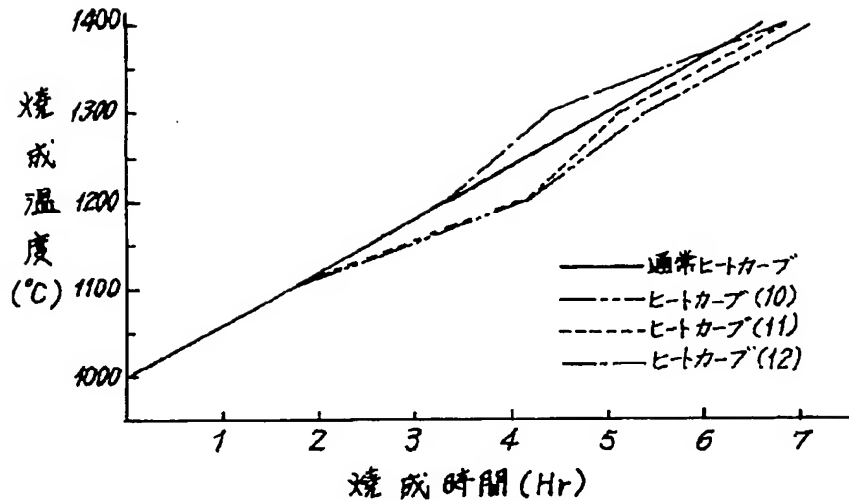
【図2】



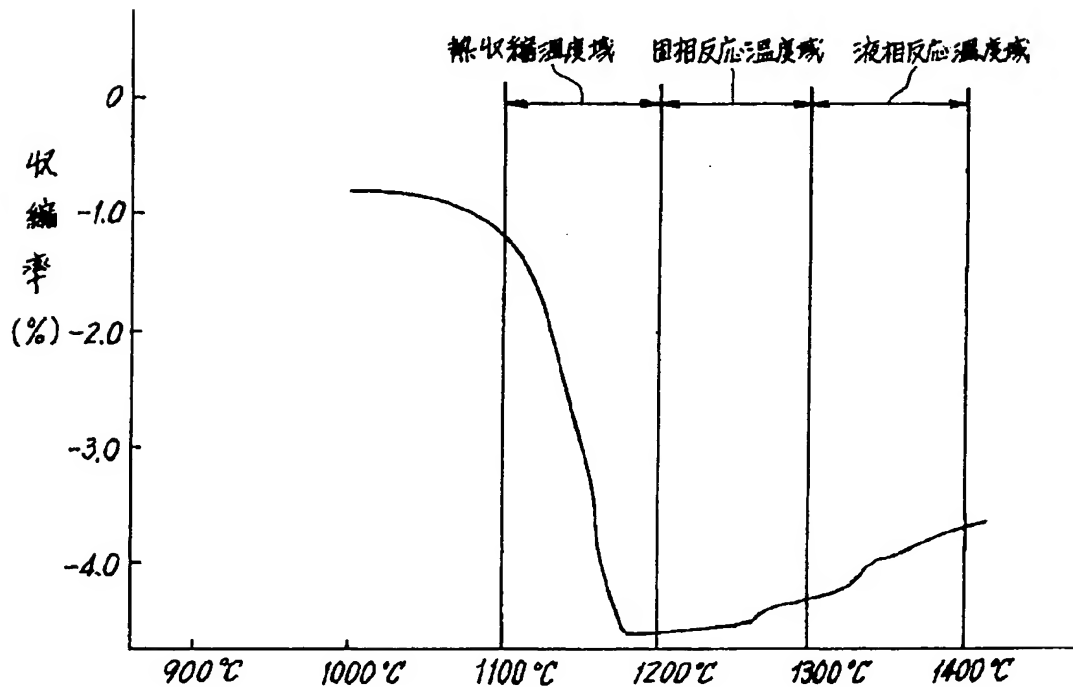
【図3】



【図4】



【図5】



【手続補正書】

【提出日】平成4年10月6日

【手続補正1】

【補正対象書類名】明細書

【補正対象項目名】0011

【補正方法】変更

【補正内容】

【0011】なお、約1100～1200℃間の糸地収縮温度域の昇温速度を60℃/Hr以下とする理由は、この温度域の昇温速度を遅くすることにより、糸地収縮がゆっくり進み緻密化するため、熱膨張率は低下する。また、緻密化

が進むことにより原料粒子間隔が小さくなり、液相反応過程でのコーゼライト化が進み易く、これによって熱膨張率が低下し、また開気孔率（吸水率）が大きくなるものと推定される。また、この収縮過程の温度域で昇温速度が80℃/Hr以上と速くした場合、成形体内部に生じる温度差により成形体に寸法、変形が発生することもあり、この点からも昇温速度を遅くすることが有効である。

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0016

【補正方法】変更

【補正内容】

【0016】まず、ハニカム成形体に対する焼成時の昇温速度の影響を調べるため、得られたハニカム成形体をマッフル窯の棚板上に載置し、表1に示すように熱収縮する約1100～1200℃温度域および固相反応が進む約1200

～1300℃の温度域および液相反応が進む約1300～1400℃の温度域における昇温速度を変えて焼成を行い、ハニカム構造体を得、得られたハニカム構造体に対し表1に示す各種特性を測定し、その影響を調べた。なお、昇温して保持温度1410℃に達した後は、この温度で4時間保持した後、降温速度150℃/Hrで降下させた。熱膨張係数はハニカム押出方向における40～800℃の熱膨張係数を測定した。吸水率は、触媒担持を行う方法の模擬として30℃の水の中に2分間ディッピングした後1cm<sup>3</sup>当たり1.4kgfの圧力空気て余分な水分を除去した後の吸水量をハニカム構造体乾燥重量に対する重量百分率：（吸水後重量－乾燥重量）／乾燥重量×100で求めた。耐熱衝撃性の評価として、各温度（700℃より25℃ずつのステップアップ）で電気炉中20分間保持した後室温に取り出した時クラックが発生し打音が濁音となった温度を求めた。結果を表1に示す。